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CHANGE OF TECHNICAL PROPERTIES OF BORIDE  
MATERIALS WITH COMPOSITION

by

H. Kotsch



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## 14. ABSTRACT

Consideration is shown on properties such as creep strength, bending strength, impact strength, hardness and oxidation resistance of sintered materials of Cr-Ni-B, Cr-Mo-B and Cr-Ti-Mo-B systems in concentration ranges 40 to 90 at percent Cr-O to 50 at percent B and 0 to 30 at percent Ni and Mo respectively. The results obtained are discussed in terms of equilibrium diagrams after Kolomytsev and his co-workers. [AT1107364]

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## CHANGE OF TECHNICAL PROPERTIES OF BORIDE MATERIALS WITH COMPOSITION

[Paper by H. Kotsch, Dresden, GDR, Presented at the International Powder Metallurgy Conference, Karlovy Vary, CSSR; 1970, Vol 4, pp 315-332]

### 1. Introduction

In the manufacture of sintered materials, on the basis of borides of the transition metals, reactions between hard material and the metallic components occur during sintering. In this case generally multiphase sintered bodies are formed.

In the following paragraphs some relationships between the properties of sintered bodies and their phase structure will be discussed.

### 2. Preparation of Samples

Specifically, materials will be studied which contain in addition the metals nickel, chromium and molybdenum or alloys on the basis nickel-chromium or chromium-molybdenum besides the borides  $\text{Cr}_2\text{B}$ ,  $\text{CrB}$ ,  $\text{CrB}_2$  and the mixed boride  $\text{CrB}_2\text{-TiB}_2$ .

The borides were made following the boron carbide process. Suitable mixtures with the additional metals or alloys were subjected to a heat treatment in hydrogen just below the final sintering temperature of the respective materials before being pressed to a test piece. This heat treatment already caused partial reactions between the components; pressing properties and sintering behavior were improved.

Final sintering of the materials -- discussed in detail in earlier publications [1-3] -- was carried out exclusively in a hydrogen atmosphere in a molybdenum furnace with titanium as a getter.

### 3. Results

#### 3.1 Materials in the System Cr-Ni-B

##### Bending-Fracture-Strength

The values for bending-fracture-strength of nickel containing chromium boride materials obtained at room temperature have been plotted in Fig. 1 on the chromium side of the isothermal cut through the ternary system Cr-Ni-B as established by Kolomycev [4] at 1000°C.

The highest values for bending-fracture-strength numbering 100 kp/mm<sup>2</sup> and higher are found in the three phase region  $\eta + \alpha + \gamma$  for materials consisting of 10-20 at. % nickel and less than 20 at. % boron.

With increasing boron content (> 20 at. %), that is, with an increasing share of Cr<sub>2</sub>B, the strength of these materials decreases steadily within this three-phase-region in order to assume values between 20 and 40 kp/mm<sup>2</sup> in the vicinity of the pure Cr<sub>2</sub>B phase.

Materials after sintering containing the higher-boron chromium-boride-phase Cr<sub>5</sub>B<sub>3</sub> (•) and CrB (•) exhibit a similar low bending-fracture-strength.

If the bending-fracture-strength of the materials is investigated at higher temperatures, a strong decrease of strength preferable as compared to the cold-bending-strength most pronounced between 700 and 980°C is found. Low melting phases or eutectics are responsible for this decrease in strength. For materials located in the three phase region  $\eta + \alpha + \delta$  the decrease of high-temperature-strength is caused above all by the eutectic occurring between nickel and the Ni<sub>3</sub>B-phase (•) at 1080°C; for sintered materials consisting of the phases  $\eta + \delta$ ,  $\eta + \delta + \gamma$ , and  $\eta + \alpha + \gamma$  principally the nickel mixed crystal as the lowest melting phase is the determinant for the behavior since it has the lowest high-temperature-strength of all phases present.

Therefore, compositions with higher nickel content lose their strength at temperatures between 700 and 980°C while for compositions with lower nickel content located in the ternary system close to the pure chromium boride phases the decrease in strength usually only takes place at temperatures above 1000°C, due to the high share of high temperature phase.

As an example, strength behavior and bending of two materials with different nickel content from the three phase region  $\gamma + \epsilon + \eta$  at various testing temperatures is shown in Fig. 2. It is seen clearly that the lock-nickel composition loses its strength only at temperatures above 1050°C.

#### Oxidation Behavior and Hardness

From Fig. 3a it can be seen that the occurrence of low melting phases also influences the oxidation behavior of the sintered materials.

Thus, materials located in the  $\gamma + \delta + \epsilon$  region which exhibits a weight increase of 2 mg/cm<sup>2</sup> and less after a 100 hour heat treatment at 950°C show weight increases already of between 10 and 15 mg/cm<sup>2</sup> at 1000°C. Increased susceptibility to oxidation and deviations occurring from the parabolic curve support the beginning appearance of a eutectic between the phases  $\gamma$  and  $\delta$ .

Increased susceptibility to oxidation of materials in the  $\gamma + \delta + \eta$  and  $\gamma + \delta$  region is not quite as clear. Here, above all the lower melting  $\gamma$ -Ni mixed crystal would oppose the formation of a dense Cr<sub>2</sub>O<sub>3</sub> protective layer; this effect appears to a higher degree for the heterogeneous materials of the three-phase-region.

The materials of the  $\gamma + \epsilon + \eta$  region are considerably more oxidation-resistant. Weight increases amount to 1 mg/cm<sup>2</sup> and less. Obviously, this good resistivity against oxidation can be explained by the presence of the  $\epsilon$ -chromium mixed crystal. Compositions containing more  $\epsilon$ -phase show the best behavior.

In Fig. 3b are plotted the R<sub>A</sub>-hardness of the materials in the ternary system Cr-Ni-B. High hardness of the materials in the  $\gamma + \epsilon + \eta$  region is conspicuous. As can be expected, materials with higher Cr<sub>2</sub>B content ( $\eta$ -phase) have higher hardness; however, compositions containing less  $\eta$ -phase (for example, 61.0 Cr, 19.6 B, 19.3 Ni, or 76.3 Cr, 12.3 B, 11.4 Ni in at. %) with . R<sub>A</sub> units show a relatively high macro-hardness. Since both materials just mentioned also exhibit micro-hardness values up to 3000 kp/mm<sup>2</sup> for individual structure components and also possess the highest values for toughness of the compositions investigated in the system Cr-Ni-B ( $\sigma_{\text{u}}$  = 80-100 kp/mm<sup>2</sup>) this group ought to claim a certain technical interest with regard to wear strength.

Since in the ternary systems Cr-Co-B and Cr-Fe-B more or less the same phase conditions are present as in the ternary system Cr-Ni-B, high-temperature strength of materials on the basis of chromium boride cannot be improved through exchange of nickel with cobalt or iron as was confirmed through our own experiments.

The high-temperature strength is limited by the occurrence of low melting phases of the binder metal with boron, or of mixed crystals with a higher content of the binder metal; therefore it cannot be expected that by changing the boride phase in the initial mixture, for example, replacement of  $\text{Cr}_2\text{B}$  by  $\text{TiB}_2$ , the high-temperature strength of the sintered materials can be increased considerably. It is therefore more favorable to use high melting metals and alloys, for example, chromium and chromium-molybdenum alloys as additions rather than the group of the iron metals.

### 3.2 Properties of Materials in the System Cr-Mo-B

The properties of the compounds in the system Cr-Mo-B investigated by us were evaluated with the aid of the chromium side of the isothermal section for this system established at  $1000^\circ\text{C}$  by Kolomycev, Moskaleva and Smetkov [5].

Fig. 4 represents the strength  $\sigma_{\text{be}}$  of the sintered material investigated at  $1200^\circ\text{C}$ . Compositions with at least 3.5 at. % molybdenum and less than 30 at. % boron have the higher values for high-temperature strength. According to the phase diagram, molybdenum is present principally as the CrMo-mixed crystal ( $\alpha$ -phase) and as the ternary CrMoB-phase of variable composition (phase T). Highest values for bending strength reaching  $80 \text{ kp/mm}^2$  and more are found in the hatched area between 15-25 molybdenum, 12-22 boron, and 55-67 chromium (at. %). This area extends into the phase regions of  $\alpha + \text{T}$  as well as  $\alpha + \text{Cr}_2\text{B}$ .

Fig. 5 shows the values for bending-fracture-strength at room temperature. As can be seen on the line of the binary region Cr-B as well as in the ternary region Cr-Mo-B, increased appearance of  $\alpha$ -Cr or the  $\alpha$ -CrMo-mixed crystals, respectively, are responsible for an increased strength.

Compositions containing more than 16 at. % molybdenum have the highest values for strength. The influence of the ternary phase T on strength can be considered to be small.

As opposed to the behavior during static testing (bending-fracture-strength), during a dynamic test of impact resistance, the strength behavior of the individual phases



as well as the influence of brittle component is more pronounced (Fig. 6). It can be proven unmistakably that the brittle boride phases  $\text{CrB}$ ,  $\text{Cr}_5\text{B}_3$  and  $\text{Cr}_2\text{B}$ , and also the ternary phase T exert a stronger influence even if there exists a certain analogy to the curve of the bending-fracture-strengths in Fig. 5. Impact strength increases with increased  $\alpha$ -chromium or  $\alpha$ -CrMo-mixed crystals, respectively, that here, too, compositions with more than 16 at. % molybdenum yield higher toughness.

Fig. 7 presents the dependence of the long-time-rupture-strength  $\sigma_{B/300}$  obtained at 1000°C from the composition. Analogous to the values for bending-fracture-strength at 1200°C, the region of higher values for long-time-rupture-strength is located approximately between 12 and 28 at. % boron and 8 to 24 at. % molybdenum. However, it can be seen from the values plotted for long time rupture strength that the highest values occur in the three phase region  $\alpha + T + \beta$ . This is very likely caused by the presence of the  $\text{Cr}_2\text{B}$ -phase; the  $\text{CrB}$ -phase and also the T-phase increase further the creep resistance due to its high melting point and its low eigen-toughness.

### 3.3 Properties of Materials in the System Cr-Ti-Mo-B

The properties, especially long-time-rupture-strength of the materials in the  $\alpha + T$  or  $\alpha + T + \beta$  region, respectively, of the ternary system Cr-Mo-B frequently can be improved by the introduction of titanium in the form of  $\text{TiB}_2$  or better yet as the mixed boride  $\text{TiB}_2\text{-CrB}_2$ .

Since titanium diboride forms a continuous series of mixed crystals with chromium diboride as well as molybdenum diboride [6], it can be assumed that the titanium will be dissolved above all in the Cr-Mo-mixed boride (phase T), that is, a mixed boride  $(\text{Cr, Mo, Ti})_x\text{B}_y$  is present. Similar relationships were also surmised by G. V. Samsonov [7].

The properties of materials in the system Cr-Ti-Mo-B have already been reported on [8].

The properties of a material of the system Cr-Mo-B are listed in Table 1 with those of two materials of the system Cr-Ti-Mo-B, which have approximately the same chemical composition except for different contents of titanium comparing the properties; it is striking too that the titanium containing materials possess higher long-time-rupture-strength, better oxidation resistance, and slightly lower bending strength at room temperature.

Creep resistance of the materials increases with increasing titanium content. A material with a higher titanium content yields the highest long-time-rupture-strength  $\sigma_B/1000$  with 24 to 25.5 kp/mm<sup>2</sup> with an elongation between 3.5 and 5.0%.

The above presentation gave a qualitative evaluation of the relationship between a few properties of the materials investigated and structure parameters. Of course, this interpretation is not complete, one reason is the presence of further magnitudes of influence which influence data, the other reason follows from the phase diagrams used for the comparison representing cuts at 1000°C which do not have to meet accurately, in each case, the relationships during the production of technical samples. Still, the considerations submitted permit some insight which is of interest for the understanding of properties of materials.

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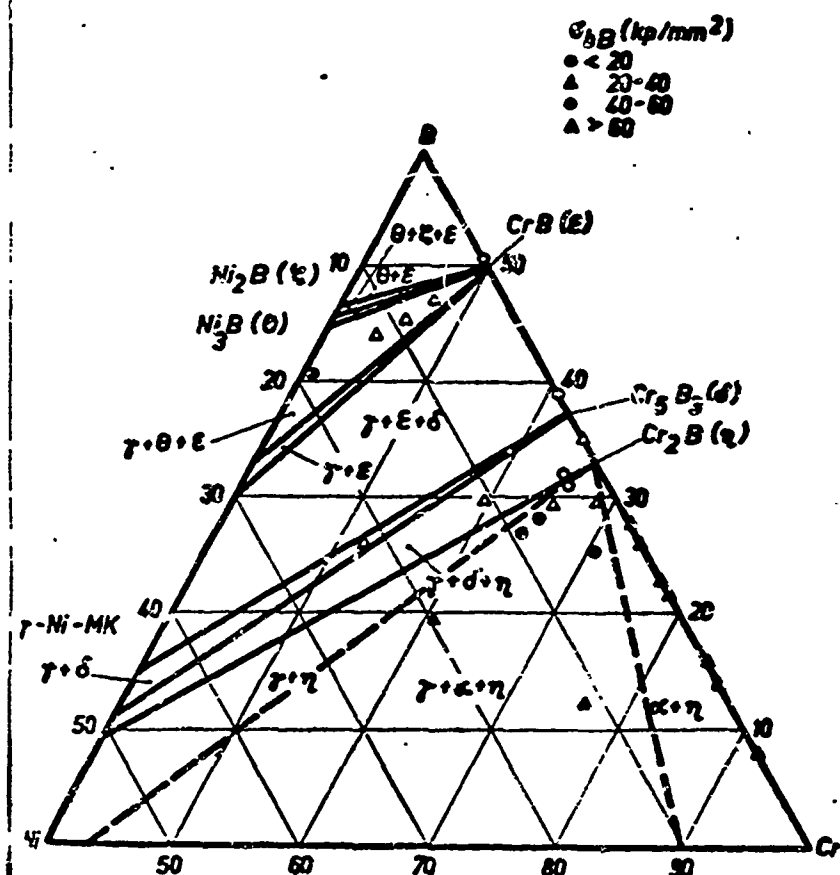


Fig. 1. Bending strength of sintered materials in the ternary system Cr-Ni-B at  $R_T$

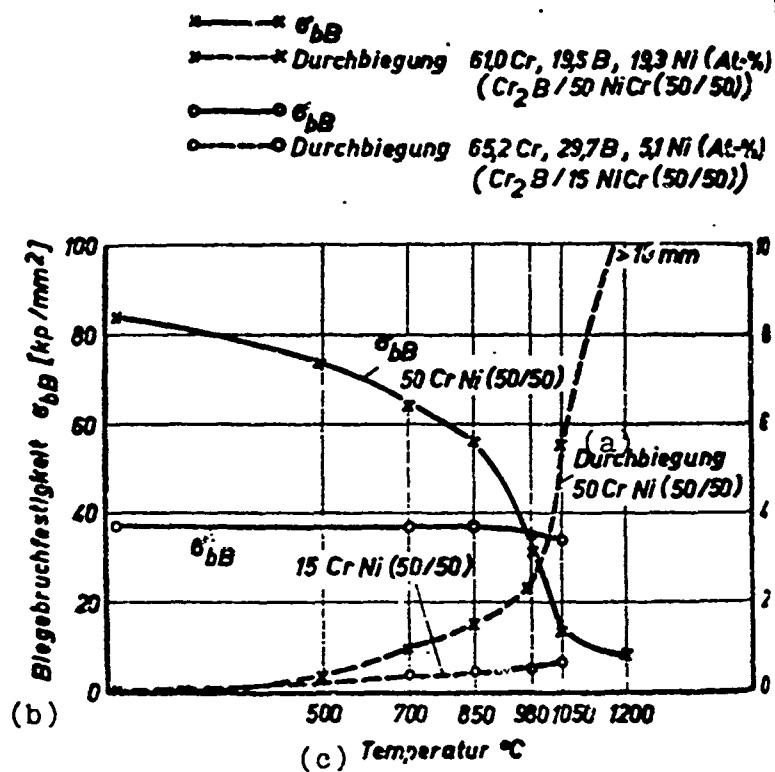


Fig. 2. Bending-fracture-strength and bending of  $Cr_2B/CrNi$  materials vs temperature

Key:

- (a) Bending
- (b) Bending-fracture-strength
- (c) Temperature

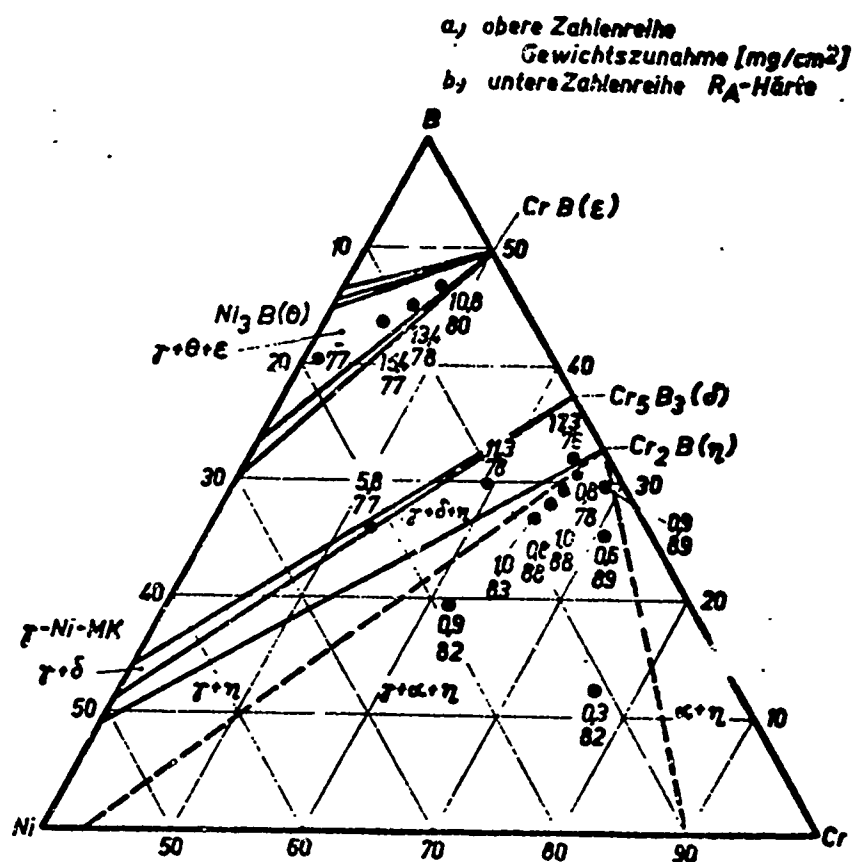


Fig. 3. Oxidation resistance (100 h, 1000°C and R<sub>A</sub>-hardness of sintered alloys (at. %) in the system Cr-Ni-B

Key:

(a) Upper series of numbers are weight increase [mg/cm<sup>2</sup>]

(b) Lower series of numbers are R<sub>A</sub> hardness

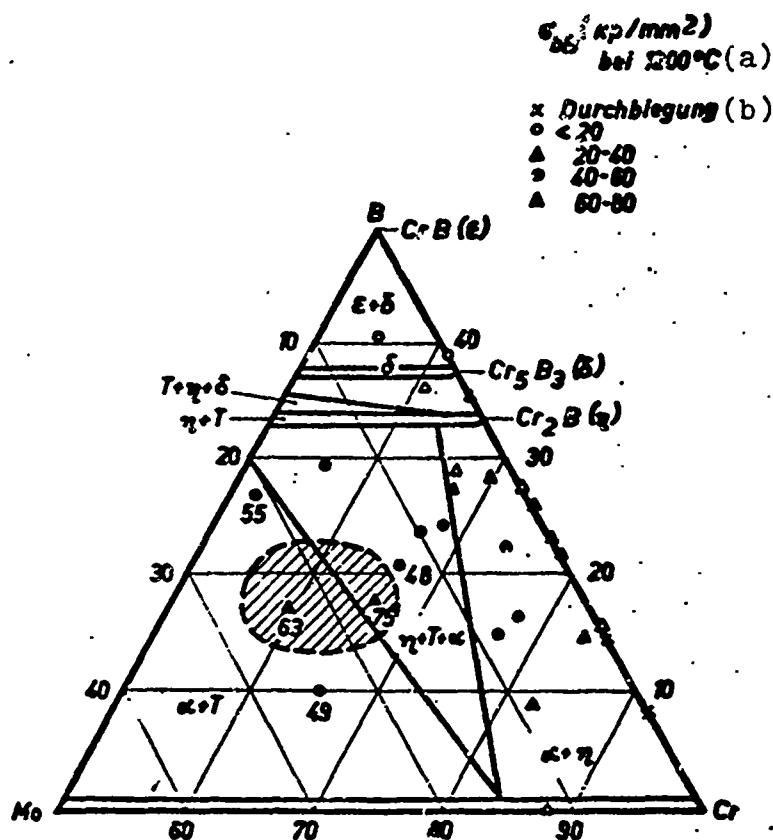


Fig. 4. Bending strength of sintered materials in the ternary system Cr-Mo-B at 1200°C

Key:

(a)  $\sigma_{bb}$  at  $R_T$  (kp/mm<sup>2</sup>) at 1200°C  
 (b) Bending

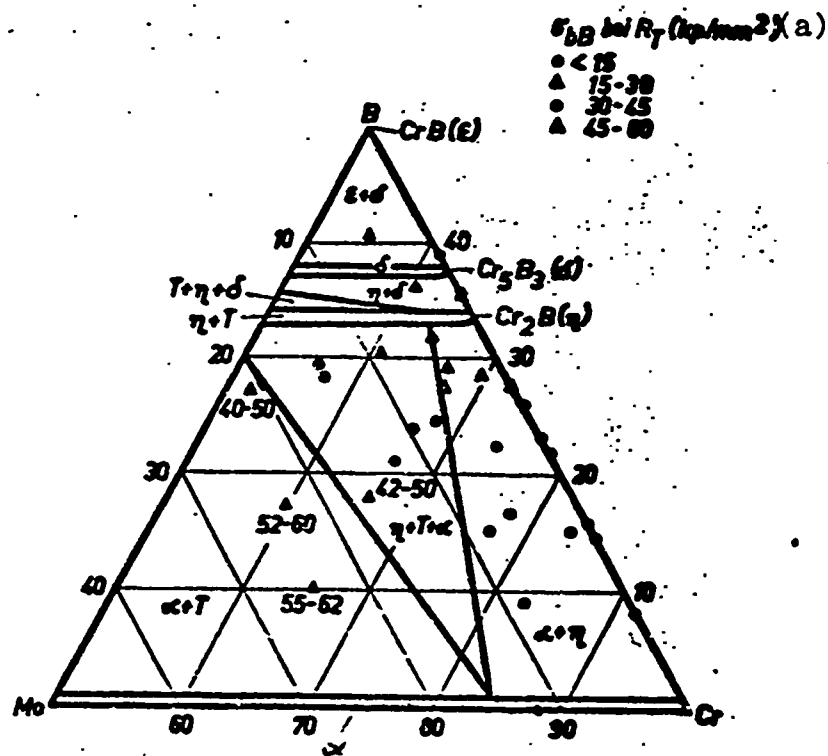


Fig. 5. Bending strength of sintered materials in the ternary system Cr-Mo-B at  $R_T$

Key:

(a) At  $R_T$

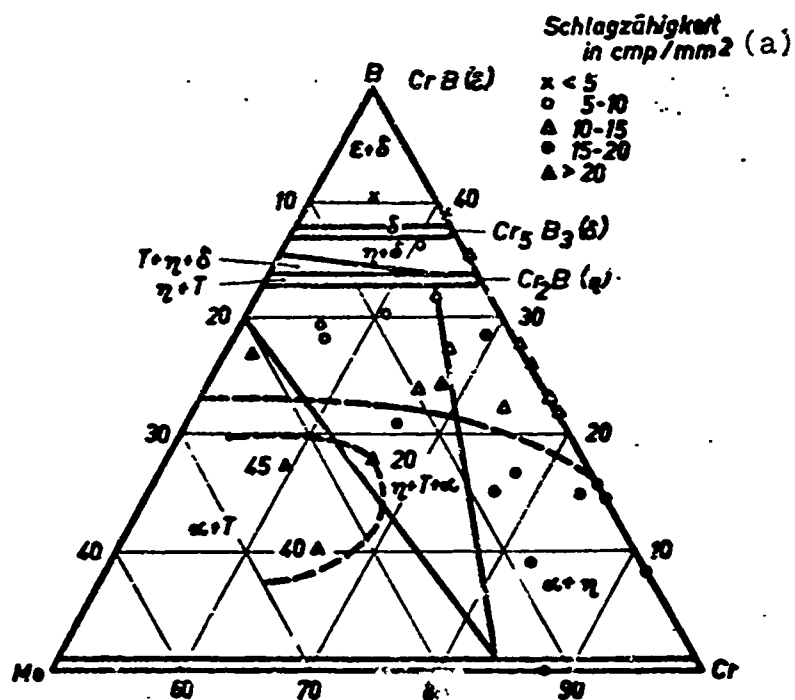


Fig. 6. Impact toughness (falling ball method) of sintered materials in the ternary system Cr-Mo-B at 20°C

Key:  
(a) Impact toughness in  $\text{cmp/mm}^2$



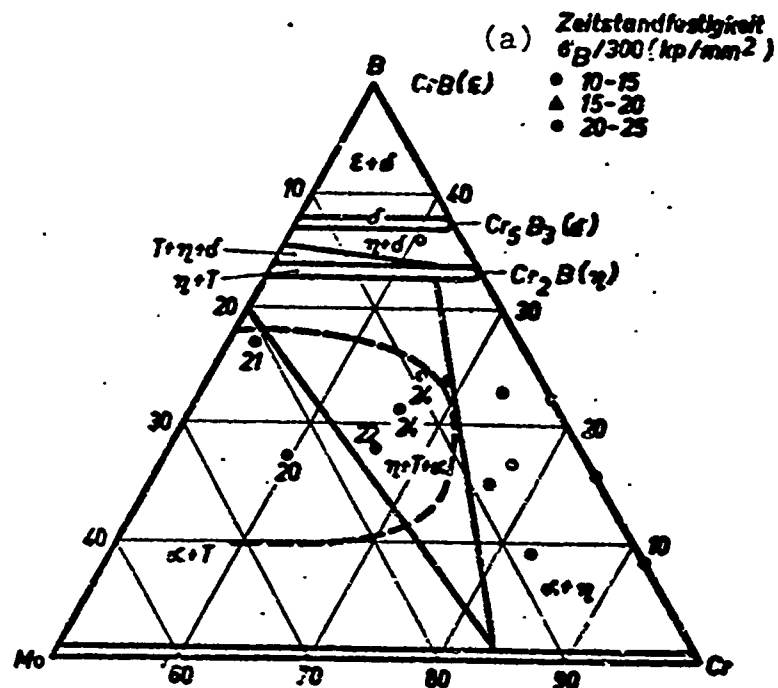


Fig. 7. Long-time-rupture-strength of sintered materials in the ternary system Cr-Mo-B

Key:

(a) Long-time-rupture strength  $\sigma_B/300$  (kp/mm<sup>2</sup>)

Table 1. Properties of Materials of the System Cr-Ti-Mo-B

## Material group

Chemical composition			
[at. %]	Cr-Mo-B	Cr-Ti-Mo-B	
Chromium	52.0	48.3	41.1
Titanium	--	3.5	10.7
Boron	27.2	27.5	27.7
Molybdenum	20.8	20.7	20.5
Density [g/cm <sup>3</sup> ]			
	7.56	7.45	7.26
Bending strength			
$\sigma_{bB}$ [kg/mm <sup>2</sup> ]			
200	40-48	34-38	32-38
9800	61-69	43-51	48-53
12000	50-60	50-60	50-60
RA hardness, 62.5 kp load			
	83.2-85.0	89.5-93.5	84.2-90.0
Increase of forging scale after 100 h at 1000°C in air [mg/cm <sup>2</sup> ]			
	1.3	0.1-0.8	
Corrosion loss in 18% HCl after 100 h at 20°C [mg/cm <sup>2</sup> ]			
		<0.5	
Long-time-rupture-strength at 1000°C [kp/mm <sup>2</sup> ]			
$\sigma_B/100$	22	24-26	25-26
Expansion [%]	1.0-3.6	0.5-3.7	0.3-0.5
$\sigma_B/1000$	20	23-25	24-25.5
Expansion [%]	10-14	5.0-10.5	3.5-5.0

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### Summary

Consideration on properties such as creep strength, bending strength, impact strength, hardness and oxidation resistance of sintered materials of Cr-Ni-B, Cr-Mo-B and Cr-Ti-Mo-B systems in concentration ranges 40-90 at % Cr, 0-50 at % B and 0-30 at % Ni and Mo respectively.

The results obtained are discussed in terms of equilibrium diagrams after Kolomytsev and his co-workers.